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Neodymium isotope analyses after combined extraction of actinide and lanthanide elements from seawater and deep-sea coral aragonite

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Key points

- **Combined extraction of Pa/U-Th-Nd from seawater and coralline aragonite**
- **Successful neodymium isotope intercalibration**
- **Reduction of sample volume requirements and workload**

Abstract

Isotopes of the actinide elements protactinium (Pa), thorium (Th) and uranium (U), and the lanthanide element neodymium (Nd) are often used as complementary tracers of modern and past oceanic processes. The extraction of such elements from low abundance matrices, such as seawater and carbonate, is however labor-intensive and requires significant amounts of sample material. We here present a combined method for the extraction of Pa, Th and Nd from 5 to 10 L seawater samples, and of U, Th and Nd from <1 g carbonate samples. Neodymium is collected in the respective wash fractions of Pa-Th and U-Th anion exchange chromatographies. Regardless of the original sample matrix, Nd is extracted during a two-stage ion chromatography, followed by thermal ionization mass spectrometry (TIMS) analysis as NdO^+. Using this combined procedure, we obtained results for Nd isotopic compositions on two GEOTRACES consensus samples from Bermuda Atlantic Time Series (BATS), which are within error identical to results for separately sampled and processed dedicated Nd samples (ε_{Nd} = -9.20 ± 0.21 and -13.11 ± 0.21 for 15 and 2000 m water depths, respectively; intercalibration results from 14 laboratories: ε_{Nd} = -9.19 ± 0.57 and -13.14 ± 0.57). Furthermore, Nd isotope results for an in-house coral reference material are identical within analytical uncertainty for dedicated Nd chemistry and after collection of Nd from U-Th anion exchange chromatography. Our procedure does not require major adaptations to independently used ion exchange chromatographies for U-Pa-Th and Nd, and can hence be readily implemented for a wide range of applications.

Index Terms: 1040, 1050, 4803, 4825, 4924

Keywords: deep-sea corals, seawater, GEOTRACES, extraction methods, neodymium isotopes

1. Introduction

The isotopes of the radionuclides protactinium (Pa), thorium (Th), uranium (U) and of the rare earth element (REE) neodymium (Nd) are invaluable tools for studying modern ocean biogeochemistry and past ocean conditions [e.g., *Goldstein and Hemming*, 2003; *Henderson and Anderson*, 2003]. Even though our understanding of their modern biogeochemical cycles is still relatively poor ^{230}Th, ^{232}Th, ^{231}Pa, and Nd isotopes (^{143}Nd/^{144}Nd ratio, expressed as ε_{Nd} = ((^{143}Nd/^{144}Nd$_{sample}$)/(^{143}Nd/^{144}Nd$_{CHUR}$) − 1) x 10,000; CHUR: chondritic uniform reservoir; *Jacobsen and Wasserburg*, 1980) are frequently used as proxies to reconstruct past ocean chemistry and dynamics [e.g., *van de Flierdt et al.,* 2012; *Anderson et al.,* 2012]. This situation is currently being rectified in the context of the international GEOTRACES program [*SCOR Working Group*, 2007] where ^{230}Th, ^{231}Pa, and Nd isotopes are 'key parameters', which have to be measured on all planned and completed GEOTRACES section cruises. However, accurate and precise analysis of these nuclides in seawater requires relatively large sample volumes (5 to 10 L) [*van de Flierdt et al*., 2012; *Anderson et al*., 2012]. Although recent analytical advances allow some laboratories to target sample volumes of less than 5 L, shipping large volumes of water to home laboratories is nevertheless an expensive endeavor. In order to reduce shipping costs and sample processing time, a combined extraction method for ^{231}Pa, ^{230}Th and Nd isotopes, which are typically analyzed by different groups, would be desirable [e.g., *Jeandel et al*., 2011].

Similarly, in paleo-archives such as deep-sea corals, sample material could be saved and time consuming sample preparation could be reduced by simultaneous separation of U, Th and Nd. The aragonitic skeleton of corals allows for accurate age control by U-series dating [e.g., *Cheng et al*., 2000], and Nd isotopes have been shown to present a promising tracer to

reconstruct past water mass properties [e.g., *van de Flierdt et al*., 2006, 2010; *Copard et al*., 2010]. Deep-sea corals are increasingly targeted as a paleoceanographic archive, as they are found in areas where other traditional archives (e.g., foraminiferal carbonate) tend to be scarce, such as the Southern Ocean, or in water depths which are undersampled by sediment cores (e.g., intermediate waters) [see *Robinson et al*., 2014 for a recent summary]. Moreover, such combined extraction approaches could ensure that the data obtained are from exactly the same sample thus facilitating optimal comparison between different geochemical parameters.

Here, we demonstrate accurate Nd isotope results obtained from a combined extraction scheme of Pa, Th and Nd from seawater and U, Th and Nd from coralline aragonite. The method is easy to adapt, as it merely requires collecting elution fractions from anion exchange columns set up for separating U-Th-Pa [e.g., *Auro et al*., 2012; *Edwards et al*., 1987], which normally would go to waste, and subsequent processing through standard ion exchange chromatography for Nd isotope analyses [e.g., *van de Flierdt et al*., 2006, 2012]. Our Nd isotope intercalibration results for the combined chemistries are in excellent agreement with results from seawater and coral samples processed for Nd only.

2. Methodology

2.1. Seawater sample preparation and anion exchange chemistry: the neodymium fraction during protactinium – thorium separation

A refined methodology to extract protactinium and thorium from large volume seawater samples was recently published by *Auro et al*. [2012]. We here briefly summarize the key features of the method (Fig. 1). Acidified seawater samples of 10 L volume were spiked (^{229}Th and ^{233}Pa) and left to equilibrate. In order to remove the trace metals of interest from the sample matrix, 100 mg of purified Fe were added per sample as $FeCl_3$. Purification of Fe

was achieved by repeated isopropyl ether extraction, and the rather high amount of Fe was chosen to quantitatively precipitate Pa [*Auro et al*., 2012]. The trace metals were isolated from solution by adjusting the pH to between 7.5 and 8.0 through addition of ammonium hydroxide to precipitate $Fe(OH)_3$. The precipitate was subsequently transferred into 50 ml Teflon® centrifuge tubes in which it was washed four times with pH-adjusted Milli-Q® H_2O (pH = 8) and then dissolved in 12 M HCl for a three stage anion exchange chromatography [*Auro et al*., 2012; Fig. 1]. Samples were loaded onto the first column (Eichrom® prefilter resin + 1X-8, 100-200 μm mesh resin) in 12 M HCl, followed by Th and REE elution in 12 M HCl, and Pa elution in 12 M HCl + 0.13 M HF. The prefilter resin hereby served to remove organic compounds from the sample solution [*Auro et al*., 2012]. The second stage targeted a purification of the Pa fraction, by repeating the first column (Eichrom® prefilter resin + 1X-8, 100-200 μm mesh). During the third stage Th and REE were separated from each other by loading the REE/Th elute from the first column in 8 M HNO_3, eluting the REE in the same acid, and collecting Th in 12 M HCl (resin: Eichrom® prefilter resin + 1X-8, 100-200 μm mesh; Fig. 1) [*Auro et al*., 2012].

2.2. Carbonate sample preparation and anion exchange chemistry: the neodymium fraction during uranium – thorium separation

Uranium-series dating of deep-sea coral aragonite (<1 g) requires thorough removal of contaminating phases prior to ion exchange chromatography and mass spectrometry. This is typically achieved by rigorous physical cleaning with a Dremel® tool and subsequent oxidative and reductive chemical cleaning [e.g., *Cheng et al*., 2000; *Robinson et al*., 2005; *van de Flierdt et al*., 2010]. Sample dissolution was achieved in nitric acid to which a mixed ^{236}U-^{229}Th spike was added [*Edwards et al*., 1987; *Hines et al*., 2015]. The samples were evaporated, then dissolved in 2 M HCl and ~3-5 mg of purified Fe were added as $FeCl_3$,

followed by addition of ammonium hydroxide to co-precipitate trace metals at pH = 7-9, whereas alkaline earth metals, and in particular Ca, are not precipitated [e.g., *Dulski*, 1996]. It should be noted that this $FeCl_3$ precipitation step would not be required for processing coral samples for Nd isotopes alone [e.g., *Crocket et al.*, 2014; *Wilson et al.*, 2014]. After a MQ rinse, samples were re-dissolved in 8 M HNO_3 for U and Th separation during two-stage anion exchange chemistry based on the recipe of *Edwards et al*. [1987]. In brief, samples were loaded in 8 M HNO_3 on Biorad® AG1-X8 (100-200 mesh) anion exchange resin, followed by matrix elution in 8 M HNO_3, which is the fraction containing the REE. Thorium is subsequently stripped off the column using 6 M HCl, evaporated to dryness and then converted to nitric form for MC-ICP-MS analyses. The U fraction was the last to be eluted from the first column using 18.2 MΩ Milli-Q® (hereafter: MQ; Fig. 1) [*Hines et al*., 2015].

2.3. Two-stage neodymium purification for TIMS NdO^+ analyses

The method for ion chromatography in preparation for TIMS NdO^+ analysis as performed in the MAGIC laboratories at Imperial College London was recently published by *Crocket et al*. [2014]. Here, we briefly summarize the key points with a focus on amendments to the published procedure. We note that for this study all Nd cuts from U-Th and Pa-Th separation were doped with ^{150}Nd after anion exchange chromatography to determine minimum Nd concentrations omitting Nd loss during sample preparation and U-Th and Pa-Th anion exchange chromatographies. It is however recommended for future work to add a mixed spike that contains Nd at an earlier stage (Fig. 1) to obtain accurate Nd concentration measurements on all samples.

Dried Nd cuts from U-Th and Pa-Th chemistries were oxidized with aqua regia at 200°C, followed by a 1:1 mixture of concentrated HNO_3 and 30% H_2O_2 prior to Nd extraction to

126 break down potential residual organics. Such residual organics may be sourced either from
127 sample matrix or from anion exchange chromatography as observed by *Auro et al*. [2012] for
128 Pa-Th separation. Subsequently, samples were converted to chloride form and redissolved in
129 1 ml 1 M HCl for cation exchange chromatography or to nitrate form for RE spec® chemistry.
130
131 **2.3.1. Step 1 - Cation exchange chemistry or TRU spec®/RE spec® chemistry: separating**
132 **rare earth elements from the sample matrix**
133 The procedure to isolate REE from sample matrix was designed to accommodate high Fe
134 content of up to ~10 mg, and was then used for REE separation from anion exchange wash
135 fractions collected from both, Pa-Th and U-Th chemistries. In order to pre-concentrate trace
136 metals ~100 mg Fe were added to each seawater sample and ~5 mg to each coral sample
137 rendering REE separation from Fe a major concern. During the first step of Pa-Th separation
138 Fe is expected to be retained by the anion exchange resin (Fig. 1). This is based on the fact
139 that Fe^{3+} has a high distribution constant K_D with strong-base anion exchange resin in
140 hydrochloric acid [*Kraus et al*., 1956], which should inhibit Fe elution with the Th/REE
141 fraction during Pa separation (Fig. 1). In praxis, small amounts of Fe are however eluted into
142 the REE fraction. During the first step of U-Th separation on the other hand, nitric acid is
143 used to achieve efficient separation of U and Th from Fe (no adsorption of Fe in 0.1 to 14 M
144 HNO_3 with anion exchange resin; *Faris and Buchanan*, 1964). Hence, the ~5 mg of Fe added
145 to coral samples will be eluted together with the REE during matrix elution so that the REE
146 fraction contains a significant Fe matrix (Fig. 1). Therefore**,** we initially applied a modified
147 version of the RE spec® [cf. *Huff and Huff*, 1993] chemistry published by *Crocket et al*.
148 [2014]. More specifically, we added 1 ml of 0.9 M ascorbic acid to 2 ml 1.5 M HNO_3 in order
149 to reduce Fe and obtain minimal adsorption onto the resin [e.g., *Horwitz et al.*, 1993]. While
150 efficient in removing Fe (tested for up to 50 mg of Fe), leaking organics from TRU/RE spec®

151 resins require strong sample oxidation after REE separation [e.g., *Gault-Ringold and Stirling*,
152 2012; *Crocket et al*., 2014; *Murphy et al.*, 2015; *Lambelet et al.*, submitted]. We therefore
153 substituted the RE spec® chemistry by traditional cation exchange chromatography [e.g.,
154 *Cohen et al.*, 1988], using 1.4 ml of pre-cleaned Biorad® AG50 W-X8 resin (200-400 mesh)
155 in hand-packed Biorad® Poly-Prep columns. Cleaning of resin and columns was done with 10
156 ml 6 M HCl, followed by resin conditioning with 1 + 0.5 ml 1 M HCl. Samples were loaded
157 in 0.5 + 0.5 ml 1 M HCl and subsequently washed in with 0.5 + 0.5 ml 1 M HCl. Sample
158 matrix was eluted with 1 + 6 ml 3 M HCl and 0.5 ml 6 M HCl, after which the REE fraction
159 was stripped off using 7 ml 6 M HCl. We chose 3 M HCl for Fe elution rather than ~3.7 M
160 HCl (i.e. the minimum K_D of Fe on AG50W-X8 resin; *Strelow*, 1960; *Nelson et al*., 1964) to
161 avoid REE loss during Fe elution. As the resin in the columns was re-used, a final wash was
162 carried out with 10 ml 6 M HCl, followed by 1 + 1 ml MQ for storage in 0.5 M HCl. Most
163 elements of relevance, and in particular barium, have K_Ds in 6 M HCl on AG50W-X8
164 [*Nelson et al*., 1964] similar to or lower than REE so that the extensive 6 M HCl wash is
165 considered sufficient to avoid cation build-up on negatively charged resin exchange spaces. It
166 is however noted that a nitric acid wash may be desirable to add [cf. *Strelow et al*., 1965].
167
168 **2.3.2. Step 2 - Ln spec® chemistry: neodymium purification**
169 Separation of neodymium (Nd) from the light rare earth elements (LREE), and in particular
170 from praseodymium (Pr) is crucial for analysis as NdO^+. We followed the method by *Crocket*
171 *et al*. [2014] and packed Savillex® columns (4 cm long, 3.2 mm inner diameter, 20 µm frits)
172 with ~320 µl Eichrom Ln spec® resin (20-50 µm) [see also *Pin and Zalduegui*, 1997]. The
173 calibration with 0.140 M HCl yielded >75 % Nd and less than 5 % Pr contribution to the Nd
174 fraction, but it is noted that Nd yields on different columns can be variable. Different to the
175 published method [*Crocket et al*., 2014], we left the Ln spec® resin in the columns between

procedural batches. Re-suspension of the resin in the column was achieved in MQ water with acid cleaned 8.3 cm long Corning® gel-loading pipette tips (1-200 µL) in order to avoid resin compaction, which could affect the precisely calibrated elution scheme, and to keep the flow rates between ~0.55 and 0.6 ml/hr. After a washing step in 6 M HCl and addition of MQ water, the resin was pre-conditioned with 0.140 M HCl and samples were loaded and later on collected in the same acid [*Crocket et al*., 2014]. The resin was re-used until degradation of separation efficiency of Nd and Pr was observed. In order to pool the Nd fraction in one spot during evaporation for subsequent TIMS NdO^+ analyses, 10 µl 0.001 M H_3PO_4 were added to the Nd fraction after Ln spec® chemistry.

2.4. Synthesizing a TaF_5 activator for TIMS NdO^+ analyses

As detailed in *Crocket et al*. [2014], samples were loaded in 2 x 0.5 µl 2.5 M HCl between two layers of 0.5 µl TaF_5 activator on degassed single W filaments in smallest possible increments in order to reduce domain mixing effects [e.g., *Andreasen and Sharma*, 2009]. During sample loading the current was set to 0.9 A and afterwards increased slowly to ~2.0 A (over a time period of 4 minutes). For this study, TaF_5 was prepared from Ta_2O_5 powder, which was fluxed in 28 M HF at 80 °C for 7 days in an acid clean Teflon beaker (10 ml 28 M HF for 250 mg Ta_2O_5) [*Charlier et al*., 2006], after which the solution was evaporated to dryness at 130°C. Per 150 mg of TaF_5 we used 0.178 ml 28 M HF, 7.98 ml MQ water, 1.025 ml 3 M HNO_3 and 0.169 ml 14.8 M H_3PO_4, which is a modified version of the recipe used by *Charlier et al*. [2006]. It is important to add the aliquot of 28 M HF first in order to dissolve the crystals either upon contact or leave until fully dissolved; otherwise the crystals remain un-dissolved once the remaining reagents are added. The combined activator and loading Nd blank was <0.2 pg. The performance of the activator was variable, similar to results reported in detail by *Crocket et al*. [2014] and *Lambelet et al.* [submitted]. We found that purification

of the activator solution by NH_4OH co-precipitation, described in the literature [e.g., *Charlier et al*., 2006] to reduce the loading blank, was not improving Nd blank levels and sometimes compromised beam intensity and stability and was hence omitted.

2.5. Thermal Ionization Mass Spectrometry

All Nd isotope analyses were carried out on a Thermo Triton TIMS at the Department of Earth Science and Engineering, Imperial College London, closely following the analytical protocol of *Crocket et al*. [2014]. Samples were routinely analyzed in nine blocks comprising 20 cycles using a peak integration time of 8.4 s at temperatures between 1520°C and 1580°C. Isobaric interferences on $^{140}Ce^{16}O$, $^{141}Pr^{16}O$ and $^{147}Sm^{16}O$ were routinely monitored for correction whereas La and in particular Ba were monitored manually. Residual Ba was however negligible in all our samples. Interference and mass bias corrections were applied as outlined by *Crocket et al*. [2014] using $^{17}O/^{16}O$ = 0.000390, $^{18}O/^{16}O$ = 0.002073 and $^{146}Nd/^{144}Nd$ = 0.7219. A slightly higher $^{146}Nd/^{144}Nd$ was applied to spiked samples [*Crocket et al*., 2014 and references therein].

Over a period of 26 months 5 and 15 ng loads of pure JNdi-1 were analyzed ($^{143}Nd/^{144}Nd$ = 0.512105 ± 0.000009, 2SD, n = 110) to monitor instrumental offset and normalize mass bias corrected $^{143}Nd/^{144}Nd$ ratios of samples to the reference ratio of $^{143}Nd/^{144}Nd$ = 0.512115 ± 0.000007 [*Tanaka et al*., 2000]. Repeated analyses of 10, 20 and 30 ng Nd loads of the USGS BCR-2 reference material yielded $^{143}Nd/^{144}Nd$ results of 0.512637 ± 0.000011 (2SD, n = 32) and 10 and 30 ng loads of our in-house coral reference material resulted in $^{143}Nd/^{144}Nd$ ratios of 0.512336 ± 0.000009 (2SD, n = 23), both of which are in excellent agreement with previously published values [*Weis et al*., 2006; *Crocket et al*., 2014]. The observed raw ratios of major interfering masses for column processed BCR-2 material and our in-house coral reference material were $^{147}Sm^{16}O/^{144}Nd^{16}O < 0.0012$, $^{140}Ce^{16}O/^{144}Nd^{16}O < 0.024$ and

226 $^{141}Pr^{16}O/^{144}Nd^{16}O < 0.46$ and hence within the suggested limits presented by *Crocket et al.*
227 [2014]. Blank levels of Nd chemistry alone were mostly <5 pg, regardless of the procedure
228 used for REE isolation. The first batch of samples processed through cation exchange
229 chemistry showed however slightly elevated Nd blanks of 7 and 17 pg for unresolved
230 reasons.
231
232 Full procedural blanks of combined U, Th and Nd separation from deep-sea corals ranged
233 from 2 to 35 pg Nd, averaging at 11 pg (n = 31) and contributed <1 % to the analyzed sample
234 Nd. This shows that the procedural Nd blank is low in the combined method although no
235 efforts were made to specifically reduce Nd blank during sample preparation and actinide
236 separation (Fig. 1). Full procedural Nd blanks of combined Pa, Th and Nd separation on
237 seawater samples reported in this study were 140 and 160 pg. The reasons for these
238 abnormally high blanks are discussed below in more detail and are related to initial problems
239 in the Pa-Th chemistry described by *Auro et al*. [2012].
240
241 **3. Application: seawater and carbonates**
242 **3.1. Intercomparison of results for Nd extraction from seawater**
243 We tested our combined Pa, Th and Nd separation procedure on filtered and acidified
244 seawater samples collected at 15 and 2000 m water depth at Bermuda Atlantic Time Series
245 (BATS) station (31°50' N, 64°10' W) from the GEOTRACES Pa-Th intercalibration
246 [*Anderson et al*., 2012]. The Nd isotope results generated for these samples are compared to
247 GEOTRACES Nd intercalibration results from samples collected independently from the
248 same water depth on the same expedition (KNR193-6/2) [*van de Flierdt et al*., 2012] (Table
249 1). The GEOTRACES Nd isotope intercalibration results for seawater from 15 m water depth
250 are $\varepsilon_{Nd} = -9.19 \pm 0.57$ and $\varepsilon_{Nd} = -13.14 \pm 0.57$ for 2000 m water depth [*van de Flierdt et al*.,

2012; Table 1]. These values are indicated by the dashed line in Figure 2 (representing the consensus values, i.e. $\Delta\varepsilon_{Nd}$ = 0). Our newly obtained Nd isotope data from the Pa-Th chemistry wash fractions are reported in Table 1 and plotted as deviation from the reported consensus values for 15 and 2000 m water depth, respectively (Fig. 2). The maximum offset of $\Delta\varepsilon_{Nd}$ is 0.06 epsilon units and demonstrates the excellent agreement between samples processed for Nd only and samples processed through the combined methodology (Fig. 1).

We should however note that the Nd data presented here were generated by the "initial method" reported by *Auro et al*. [2012]. This method suffered from procedural problems during column chemistry resulting in higher Th blanks and lower Th yields [see *Auro et al*., 2012 for details]. Neodymium and Th are eluted from the same column (Fig. 1), and we can see this reflected in elevated Nd blanks of up to ~2 %, paired with estimated sample loss of up to 72 % (Table 1) when compared to expected seawater Nd concentrations from published Nd results [*van de Flierdt et al*., 2012]. As our TIMS NdO^+ method allows for analyses of sub-nanogram levels of Nd, we were however able to isotopically constrain the Nd blank from these samples, i.e. 0.14 ng Nd with ε_{Nd} = -19.31 ± 0.78 and 0.16 ng Nd with ε_{Nd} = -10.49 ± 0.69. These values are used for a mixing calculation to assess the significance of blank contamination to our BATS seawater Nd results.

$$IC_{sample} = \frac{IC_{final} \times \left([Nd]_{sample} \times f_{sample} + [Nd]_{blank} \times f_{blank}\right) - IC_{blank} \times [Nd]_{blank} \times f_{blank}}{\left([Nd]_{sample} \times f_{sample}\right)}$$

IC stands for the isotopic composition, [Nd] for the Nd concentration, and f for the fraction. Following above mixing equation we can calculate that the maximum Nd blank contribution of 160 pg would shift the sample Nd isotopic composition by 0.01 epsilon units. Such blank contribution is considered negligible, supported by the accurate results we report for the Nd isotopic compositions from Pa-Th wash fractions (Table 1, Fig. 2).

3.2. Intercomparison of results for Nd extraction from aragonitic deep-sea coral skeletons

The application of combined uranium, thorium and neodymium extraction from aragonitic sample matrices was tested on a coral reference material created from a homogenized mixture of *Desmophyllum dianthus* deep-sea corals from the Southern Ocean (in-house coral reference material) [see *Crocket et al*., 2014 for details]. Neodymium yields for the Fe co-precipitation and U-Th anion exchange chromatography were found to be nearly quantitative at 88-90 % during three individual batches of chemistry, consistent with 'slight adsorption' of Nd on anion exchange resins in HNO_3 [*Faris and Buchanan*, 1964]. Such Nd yields are likely representative for the Pa-Th separation as well, considering that there is no adsorption of Nd on strong-base anion exchange resins in HCl minimizing Nd loss on the first column [*Kraus and Nelson*, 1958] (Fig. 1). Hence, the matrix elution with HNO_3 on the second column of Pa-Th separation is considered to be the only place where minimal loss of Nd could occur, resulting in similar quantitative Nd yields for both anion exchange based chemistries, i.e. U-Th and Pa-Th separation [cf. *Kraus and Nelson*, 1958; *Faris and Buchanan*, 1964].

In order to test our combined U-Th-Nd separation for accuracy of Nd isotopes, we report results on 20 repeats of our in-house coral reference material (10 and 30 ng Nd aliquots) processed individually through RE spec® chemistry (n = 11) and cation exchange chemistry (n = 9) (Table 1; Fig. 3). These results are compared to Nd isotope data obtained from three coral reference material aliquots (30 ng Nd each; Table 1) processed individually through Fe co-precipitation and U-Th anion exchange chromatography. The results document excellent reproducibility of coral reference material aliquots regardless of the applied procedure. In particular, results are consistent between samples collected from U-Th chemistry wash

fractions, those loaded directly onto the respective first column of Nd extraction, and previously published coral reference material Nd isotope data [*Crocket et al*., 2012] (Fig. 3, Table 1). Together with previous work [cf. *Jeandel et al*., 2011], these results highlight the benefit of combined procedures to separate different elements from the same sample, and moreover, show the potential to extend the range of extracted elements.

4. Summary and concluding remarks

We here presented intercalibration Nd isotope results of combined separation procedures for Pa, Th and Nd from seawater, and U, Th and Nd from aragonitic sample matrices. The method was designed with minor modifications to existing protocols used in separate laboratories carrying out U-Th-Pa and Nd isotope analyses as it utilizes wash fractions from U-Th and Pa-Th anion exchange chemistries that are then further processed for Nd separation. The method significantly reduces the workload and sample consumption for common applications in low temperature geochemistry and is easy to implement between different laboratories.

We tested the combined methodology for Nd isotope accuracy and obtained excellent results compared to previously published data for Nd isotope processing alone. Future optimization of our combined approach can be obtained by separation of additional elements from the same samples and inclusion of a mixed Nd-Th-Pa and/or Nd-U-Th spike prior to Fe co-precipitation in order to generate quantitative Nd concentration data from the same samples.

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Table 1: Neodymium isotope results for BATS seawater and a deep-sea coral reference material grouped by chemical procedure applied.

Sample	$^{143}Nd/^{144}Nd$	2SE	ε_{Nd}	2SE	2SD	Nd in wash fraction (ng)	Pre-chemistry Nd (ng)
Seawater samples (this study)							
KNR193-6-Th-720 (BATS 15 m)	0.512167	0.000006	-9.20	0.13	0.21	7.5	20.7
KNR193-6-Th-648 (BATS 2000 m)	0.511965	0.000007	-13.12	0.13	0.21	8.0	25.9
KNR193-6-Th-649 (BATS 2000 m)	0.511965	0.000010	-13.14	0.20	0.21	9.2	25.9
KNR193-6-Th-650 (BATS 2000 m)	0.511968	0.000008	-13.08	0.16	0.21	7.3	25.9
Seawater samples of published consensus values from 14 laboratories [van de Flierdt et al., 2012]							
GEOTRACES BATS 15 m	0.512167	0.000029	-9.19		0.57		
GEOTRACES BATS 2000 m	0.511964	0.000029	-13.14		0.57		
In-house deep-sea coral reference material (this study)							
Coral Ref 1 (U-Th fraction)	0.512337	0.000004	-5.87	0.08	0.18	26.68	29.72
Coral Ref 2 (U-Th fraction)	0.512332	0.000004	-5.97	0.07	0.18	26.64	29.81
Coral Ref 3 (U-Th fraction)	0.512336	0.000004	-5.89	0.08	0.18	26.23	29.77
Coral Ref RE spec® (n = 11)	0.512337	0.000009	-5.89		0.19		
Coral Ref AG50W-X8 (n = 9)	0.512335	0.000009	-5.90		0.18		
In-house deep-sea coral reference material [Crocket et al., 2014]							
Coral Ref (n = 13)	0.512338	0.000008	-5.86		0.16		

456 **Table 1: Neodymium isotope results for BATS seawater and a deep-sea coral reference**
457 **material grouped by chemical procedure applied.** Neodymium isotope results for Pa-Th
458 anion exchange chemistry wash fractions are based on BATS GEOTRACES Pa-Th
459 intercalibration samples (KNR193-6-Th). 'Neodymium in wash fraction' refers to the amount
460 of Nd in the respective anion exchange chemistry wash fractions, determined by ^{150}Nd doping
461 after collection. The pre-chemistry Nd content is estimated based on the $[Nd]_{seawater}$ at BATS
462 from *van de Flierdt et al*. [2012]. Neodymium results on our in-house coral reference
463 material, processed through combined U-Th-Nd chemistry, are listed individually (n = 3);
464 REE were isolated using cation exchange chemistry. Pre-chemistry Nd amounts were
465 determined by weighing of an aliquot of dissolved in-house coral reference material of
466 known Nd concentration. Results for in-house coral reference material are grouped according
467 to chemical procedures applied, i.e. RE spec® chemistry (n = 11) and cation exchange
468 chemistry with Biorad® AG50W-X8 resin (n = 9). All in-house coral reference material
469 aliquots were taken from the original solution prepared from homogenized deep-sea coral
470 powder by *Crocket et al*. [2014]. Literature GEOTRACES and coral reference material data
471 taken from *van de Flierdt et al*. [2012] and *Crocket et al*. [2014]. 2SE is the analytical 2σ
472 standard error. 2SE for Nd concentrations is ≤ 0.005. 2SD is the external long term 2σ
473 standard deviation. Seawater results from this study are shown with the 2SD obtained from
474 repeated analyses of BCR-2 rock reference material (see section 2.5). In the case of the

475 GEOTRACES BATS results, 2SD represents the 2σ standard deviation of the 14 laboratories
476 involved in the respective measurements [*van de Flierdt et al*., 2012].
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Figure 1: Working scheme of combined Pa-Th-Nd and U-Th-Nd chemical procedures towards Nd isotope analyses.

480 **Figure 1: Working scheme of combined Pa-Th-Nd and U-Th-Nd chemical procedures**
481 **towards Nd isotope analyses.** Purified U, Pa and Th fractions were analyzed by MC-ICP-
482 MS [*Anderson et al*., 2012; *Auro et al*., 2012; *Hines et al*., 2015]. Note that some laboratories
483 apply a second Th purification step during U-Th separation [cf. *Burke and Robinson*, 2012].
484 It is also noted that isotopic spiking is not yet tested for the combined method in seawater and
485 corals. It has however successfully been achieved for combined Pa-Th-Nd chemistry of
486 marine particulate samples (Kretschmer, Lambelet et al., pers. comm.). Finally, our preferred
487 method for REE separation after Fe co-precipitation and actinide extraction is the traditional
488 cation exchange chemistry, as the application of strong oxidizing agents to combat leaking
489 organics from such resins can be avoided [e.g., *Lambelet et al.*, submitted].
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Figure 2: Neodymium isotope results obtained for wash fractions from anion exchange chemistry further processed for Nd separation on GEOTRACES BATS seawater Pa-Th intercalibration samples.

492 **Figure 2: Neodymium isotope results obtained for wash fractions from anion exchange**
493 **chemistry further processed for Nd separation on GEOTRACES BATS seawater Pa-Th**
494 **intercalibration samples.** Data are presented as $\Delta\varepsilon_{Nd}$ deviation from GEOTRACES Nd
495 intercalibration results from 14 laboratories (dashed line) [*van de Flierdt et al*., 2012].
496 Numbers represent consensus values and the grey shading indicates the 2SD.
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Figure 3: In-house coral reference material Nd isotope analyses of sample loads containing 10 and 30 ng Nd, measured over a period of 26 months.

Figure 3: In-house coral reference material Nd isotope analyses of sample loads containing 10 and 30 ng Nd, measured over a period of 26 months. Error bars of individual measurements are given as internal 2SE. Sample loads containing 10 ng of Nd are indicated by white symbols with black outline. The first 20 results (diamonds and squares) were obtained for samples processed through Nd isotope chemistry only, using Eichrom RE spec® resin (with and without addition of ascorbic acid) and cation exchange chemistry, respectively, to isolate REE from the sample matrix. Black circles mark results obtained by processing the same coral reference material through Fe co-precipitation and U-Th anion exchange chemistry followed by Nd isotope separation (i.e. the combined method). The long term average of all results is $^{143}Nd/^{144}Nd = 0.512336 \pm 0.000009$ (n = 23) and the grey shading marks the 2SD. The grey triangle marks the results previously published by *Crocket et al*. [2014] on the same in-house coral reference material.